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A study on the depth distribution of melamine in polyester-melamine clear coats

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ABSTRACT

The depth distribution of melamine in polyester-based coatings was investigated by XPS (X-ray photoelectron spectroscopy) as well as Raman analysis on cryo-ultra-low-angle microtome (cryo-ULAM) prepared coatings on hot dip galvanized (HDG) steel panels. Additionally, free standing films were analyzed on the air/coating and the coating/substrate interfaces: for polyester/melamine ratios ≤ 20 wt.% the melamine concentration was equal on both sides of free films, which is in accordance with literature. This finding could not be confirmed for the coatings applied on HDG steel panels that revealed a higher amount of melamine in the surface-near region. In addition various types of non-linear melamine concentration gradients have been detected over depth by XPS as well as Raman spectroscopy. This behavior was confirmed for all types of coatings irrespective of binder chemistry and curing temperatures in the range of 220–260°C. Whereas previous studies have mainly focused on higher melamine concentration where gradient properties are more pronounced, this work tries to fills the gap towards lower melamine contents, which are of greater relevance for industrial coatings. According to these results, a qualitative model on the melamine distribution has been established, which explains the observed non-linear gradients on the basis of transport phenomena and crosslinking kinetics within the curing process. This model is also in agreement with experimental findings from previous works.

1. Introduction

Hexamethoxymethylmelamine (HMMM) is a multifunctional crosslinker and commonly used for industrial thermoset coatings commonly applied in the automotive, appliance and construction industries [1–5]. Hence, it is crucial for the crosslink density in the final coating. It is known for its tendency to undergo self-condensation via two alkylated moieties or two methylol groups, which are expected to occur at temperatures above 150°C [6]. The co-condensation reaction, which involves the hydroxy functionalities of the resin, was shown to proceed faster at lower curing temperatures [7,8]. The reaction mechanism is generally well understood [6,9] and the reaction is usually accelerated by strong acid catalysts, e.g., sulfonic acids [9].

Turning to physical and chemical aspects such as crosslink density, hardness, flexibility, micro-structural appearance and adhesion, the number of published work is still manageable. In this context the final HMMM distribution in polyester/HMMM coatings, which influences the above mentioned properties, is of great interest and has been discussed in earlier work: *Hirayama and Urban* [10] investigated the HMMM distribution in polyester/HMMM coatings by means of Attenuated Total Reflectance Fourier Transform Infrared (ATR FT-IR) spectroscopy and they showed that a low OH-value, high curing temperatures and a HMMM amount of ~30 wt.% leads to the formation of HMMM enrichment at the air/film interface. *Zhang* et al. [11,12] used Confocal Raman Spectroscopy and nanoindentation to study the self-condensation of HMMM in an aliphatic polyester/HMMM clear coating. They reported on spherical HMMM clusters in the size of about 5 μm, which are attributed to the auto-condensation of HMMM. Recent published results [13] have shown that the HMMM molecules have a tendency to agglomerate around the polar sections of the polyester resin such as the hydroxyl groups and possibly ester linkages. *Lowe* et al. [14] suggested that HMMM preferentially reacts with the pretreatment of the substrate, which ought to mean a migration of those molecules towards the pretreated metal/coating interface. *Perruchot* et al. [15] performed angle-resolved XPS (X-ray Photoelectron Spectroscopy) on the top surface of linear and branched polyester/HMMM coatings containing

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silicone and acrylic based flow additives. They showed that a preferential segregation of the additives towards the air/coating interface is responsible for the formation of an outerlayer. *Hamada* et al. [16] investigated thin films (~1 μm) by ATR analysis. They found that below a certain value of the HMMM/polyester weight ratio, no HMMM enrichments at the coating surface can be expected independent on the type of polyester.

A further work, which has to be mentioned, is the study of *Gamage* et al. [17], who investigated aromatic polyester/HMMM free films by XPS on the top and the bottom side of the films. HMMM segregation has been explained in terms of concentration gradients of unreacted HMMM moieties, the period in which they can diffuse until they are trapped by condensation reactions influenced by the diffusion coefficient and the heating rate. Additionally, they determined that for HMMM concentrations below or equal 20 wt.% no surface HMMM enrichment can be expected. According to the comparison of these publications it becomes clear that there is still a need for further investigation on polyester/HMMM systems, despite the formation of a high concentration surface HMMM layer seems to be uncontroversial under certain experimental conditions, which in large parts do not apply to industrial relevant conditions, e.g., the high amount of HMMM (e.g., 30 wt.% or even higher) [10,17] in the formulation, extended curing temperatures and dwell times (e.g., 250°C for 1 min) [10].

Hence, our study was intended to narrow the gap between, firstly extended experimental parameters, which clearly reveal the distinct physical and/or chemical properties and secondly the industrial specific factors. The majority of work done in this field to date has been based on free standing films. Consequently such free films have also been used as a starting point for our study to correlate the newly introduced coatings, covering aliphatic as well as aromatic polyester resins, with former findings. Additionally coatings applied on hot-dip galvanized (HDG) steel panels were investigated since only this form is of practical relevance. To reveal the chemical structure over the entire coating depth, a new technique of cryo ultra-low-angle microtomy (cryo-ULAM) in combination with XPS has been applied for this purpose. This approach has already proven successful to perform depth profiling of organic coatings applied on HDG steels with coating thicknesses between 2 and 20 μm [18,19], since it turned out that even modern sputter techniques like Argon cluster and C_{60} are not appropriate for such profiling tasks. As a complementary method Raman spectroscopy on a sample cross section was done, to confirm the result of XPS depth profiling.

2. Experimental section

2.1. Materials

All clear coats were provided by Becker Industrial Coatings Ltd (Liverpool/UK). The HDG panels experienced an alkaline cleaning with a freshly prepared solution of Ridoline C72W (bath temperature: 45°C; pH: ~12.8; dwell time: 30 s). Subsequently they were rinsed with deionized water and finally dried. Liquid coatings were applied on the cleaned HDG panels according to a standard procedure in the laboratory of voestalpine Stahl (Linz/Austria) using a spiral wound wire draw bar and adjusted to finally reach a dry film thickness of ~20 μm. Panels were cured to peak metal temperatures (PMT) of 220°C, 240°C and 260°C at an oven temperature of 300°C (recirculating air) with dwell times of 30 s, 37 s and 48 s, respectively. Afterwards the panels were immediately quenched in deionized water. For analysis purposes pieces of approximately 15 × 4 mm in size were punched out.

Free standing films were produced by applying the clear coats likewise on polytetrafluoroethylene (PTFE) release coated panels. These panels were cured to a PMT of 240°C and air cooled by placing them on a solid steel block. Coating films were removed from the PTFE coated substrate immediately before XPS analysis.

This work considers three different coating compositions as specified in Table 1 (including abbreviations for each system). The binders used are representative for resins used in the coil coating industry covering a linear aromatic type (**L220**, **L240** and **L260**), a branched aromatic one (**B220**, **B240** and **B260**) and finally an aliphatic coating (**A14**, **A20** and **A24**). The aliphatic resin has been formulated with different polyester/HMMM ratios in order to estimate the influence of increasing HMMM concentrations. For all liquid formulations an amine blocked *p*-toluenesulfonic acid (pTSA) was employed as a catalyst.

Table 1
The coating formulations, polyester/HMMM ratios and curing conditions.

code	type	OH Number	polyester/HMMM ratio	PMT [°C]
L220	aromatic/linear	5	86/14	220
L240	aromatic/linear	5	86/14	240
L260	aromatic/linear	5	86/14	260
B220	aromatic/branched	50	86/14	220
B240	aromatic/branched	50	86/14	240
B260	aromatic/branched	50	86/14	260
A14	aliphatic	35	86/14	240
A20	aliphatic	35	80/20	240
A24	aliphatic	35	76/24	240

2.2. Methods and sample preparation

2.2.1. X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed on a commercial ThermoFisher (East Grinstead, UK) Theta Probe system equipped with a monochromated Al-K_{α} X-ray excitation (1486.7 eV) source. The setup employs a dual flood gun system for charge neutralisation, which simultaneously provides Ar^{+} ions and low kinetic energy electrons (1–2 eV) to the sample surface. The hemispherical analyser was operated in the constant analyser energy (CAE) mode and the pass-energy (PE) was set to 200 eV for a survey spectrum. For a high resolution (HR) spectrum a PE of 50 eV was selected. This value ensures a high spectral intensity at a suitable signal-to-noise-ratio. The spot size (diameter) was set to 200 μm, respectively in order to accomplish a compromise between the final depth resolution, good spectra quality and acceptable short acquisition times. The survey spectra were acquired with an energy step of 1 eV and the HR data with 0.05 eV. The manufacturer's software package Avantage was used for quantitative elemental and chemical data assessment. For that purpose a modified Shirley background – the so-called Smart background – was used, employing an additional constraint that the iteratively adjusted background is finally not of greater intensity than the actual data at any point in the region. To avoid that the background is greater than the data, the background is set to follow the data and the effective start point of the Shirley-type background is moved further inside the defined region [20].

Scofield sensitivity factors were used for data normalization. The XPS line scans were performed on the microtomy prepared wedge-shaped tapers with a step size of 200 μm resulting in a final depth resolution of ~3 μm for the organic coating with a thickness of ~20 μm.

2.2.2. Raman spectroscopy

The Raman data was collected with a Witec α 300R confocal setup equipped with a green laser (λ = 532 nm; a frequency doubled Nd:YAG laser; 29.7 mW of laser power) and a thermo electric cooled back-illuminated CCD detector. Data was collected at 1 μm below the sample surface with 10 accumulations per position and an integration time of 0.23 s. The piezo-electric regulated scan table is movable with a stepper motor. The measurements were performed with a 60x/NA = 1.0 water immersion objective to minimize burning as well as fluorescence effects. For all data a wavenumber correction was achieved from a silicon reference. Raman analysis performed in terms of a mapping on the sample cross section. For that purpose a piece of ~15 × 4 mm in size